

BIOMASS LIQUEFACTION UTILIZING EXTRUDER-FEEDER REACTOR SYSTEM

Don H. White, D. Wolf and Y. Zhao

Department of Chemical Engineering, University of Arizona, Tucson, Arizona 85721

ABSTRACT

Biomass including wood could provide liquid fuels on a regional basis if an economic liquefaction process can be developed. Through research sponsored by the U.S. Department of Energy (DOE), under its Thermochemical Conversion Program managed by Battelle PNL, the University of Arizona has developed a unique method of pumping concentrated, viscous biomass slurries, characteristic in biomass direct liquefaction systems. A modified single-screw extruder has now been shown to be capable of pumping solid slurries as high as 60 wt. % wood flour in wood oil derived vacuum bottoms. Preliminary experimental runs showed that a low-oxygen crude wood oil could be produced over a wide range of temperatures, pressures, with or without carbon monoxide and with or without a sodium carbonate catalyst.

INTRODUCTION

The modified extruder has now been shown to be capable of pumping slurries as high as 60 wt. % wood as compared to only 10-20 wt. % in conventional systems. The ability to handle such concentrated slurries which are in solid form at normal temperatures is expected to improve direct liquefaction wood oil quality and process economics. Various preliminary process design and economic studies indicated that the utilization of this newly-developed extruder-feeder in biomass direct liquefaction processes could lead to one or more of the process improvements listed below.

1. Elimination of recycle wood oil (or dramatically reducing it), which should result in less coke formation and better quality wood oil. In fact, even the reduced recycle will be wood oil vacuum bottoms, a heavy residue that might be decomposed further to a lighter oil.
2. Attainment of reactor temperature almost instantaneously, by the mode of adding heat (some by extruder-feeder preheater and remainder by superheater steam).
3. Attainment of near-plug flow in the reactor when using static mixers. This means that all biomass solids with nearly the same residence time in the reactor, have better control of conversion per pass and more uniform wood oil quality should be attained.

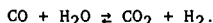
The extruder-feeder acts simultaneously as both a feed preheater and a pumping device into a 3,000 psi pressure reactor in the biomass liquefaction process. It could prove to be of importance in other processes where high concentration of solids in liquids are to be handled, like in the pulp and paper industry, hydrolysis of wood or other cellulose, other biomass liquefaction processes, coal liquefaction processes and some biomass gasification processes.

EARLY BUREAU OF MINES RESEARCH

In the early 1970's the Bureau of Mines showed that cellulosic materials, all other carbohydrates, wood wastes (largely cellulose and lignin), urban wastes (mostly cellulose plus other carbohydrates, proteins, fats, and small amounts of other organic materials), sewage sludge, agricultural wastes, and bovine manure can be converted to oil with carbon monoxide and water. Some plastics depolymerize and dissolve in the product oil; some remain as part of the unconverted residue (1,2).

Effect of Carbon Monoxide

Carbon monoxide and water react to form hydrogen and carbon dioxide in the following water-gas shift reaction:



Because some hydrogen adds to cellulose during its conversion to oil, it seemed at first reasonable to suppose that the hydrogen gas formed in the water-gas shift was responsible for converting cellulose. But when hydrogen was added to the reactor, it had little effect; an equivalent molar amount of carbon monoxide was much more effective. Early work showed that carbon monoxide consumption at lower temperatures (250°C) was low.

Effect of Water

The original experiments by the Bureau of Mines with carbon monoxide on low-rank coal (lignite) were successful without added water, because this coal has a large amount of moisture. However, addition of water was beneficial. It served as a vehicle (solvent) for the reaction. Cellulose forms water on being heated and the added water plus carbon monoxide improves the oil yield. However, added water also shifts the water-gas reaction in the direction of more carbon dioxide and hydrogen (more carbon monoxide is consumed); this side reaction may or may not be desirable.

The critical temperature of water is 375°C; above this temperature all the water is in the gaseous state. There were indications that the presence of liquid water is desirable. This may be accomplished by adding enough water so that some liquid is always present. The temperature must of course be below 375°C. If insufficient water is added, most of it will be in the gas phase, even below 375°C.

Nature of Conversion Reactions

The Bureau of Mines speculated on the possible chemical reactions in 1971 as follows:

"Cellulose, starch, and other carbohydrates can undergo a large number of reactions on treatment at elevated temperatures and pressures with carbon monoxide, water, and sodium carbonate or other alkaline salts. Since almost every carbon atom in a carbohydrate is bonded to an hydroxyl group (-OH), some dehydration will take place. Hydrolyses of the polysaccharides to glucose will also occur; glucose and the smaller units formed from it are soluble in water. Hydrolysis of the fats in the refuse to long-chain palmitic and stearic acids will also occur. Probably the most important overall reaction in converting cellulose to oil is the splitting out of oxygen to form molecules with high hydrogen-to-carbon ratios. Cellulose and other carbohydrates lose water and carbon dioxide just on being heated. Oxygen can also be lost by reaction with the added carbon monoxide to form carbon dioxide, by hydrogenation, by various disproportionation reactions, and by combinations of these reactions".

Later Bureau of Mines Research

Further research work in the early 1970's by the Bureau of Mines resulted in data on the reaction parameters (1). In general, the more readily hydrolyzable forms of cellulose, especially those containing pentosan units can be readily converted to a bituminous oil at temperatures as low as 250°C. Lignin and high-molecular-weight cellulose, containing crystalline cellulose, required higher reaction temperatures of about 350°C.

Wood is considerably more difficult to convert to oil than other biomass sources, but good oil yields were obtained by the Bureau of Mines in the presence of organic solvents as shown in Table 1 during wood liquefaction at 275°C. It was believed that some carbon monoxide was evolved during the decomposition of the wood and was apparently about equal to the amount of carbon monoxide consumed.

Table 1. - Effect of Water and Solvent on Wood Liquefaction

(50 g softwood sawdust, 1 hr at 275°C, 300 psig CO)

| Cresol solvent, (g) | Water, ml | Catalyst | | Pressure, psig | Conversion pct | Yield, pct | CO used g/100 g wood |
|---------------------|-----------|---------------------------------|--------|----------------|----------------|------------|----------------------|
| | | Type | Amount | | | | |
| 50 | 200 | HCO ₂ Na | 5 | 1,900 | 99.9 | 48 | 6 |
| 50 | 50 | Na ₂ CO ₃ | 2 | 1,780 | 99.3 | 60 | 4 |
| 75 | 10 | None | 0 | 1,470 | 99.0 | 58 | 0 |
| 75 | 10 | HCO ₂ H | 1 | 1,500 | 99.3 | 58 | 0 |
| 75 | 10 | HCO ₂ Na | 1 | 1,560 | 99.8 | 60 | 0 |

The Bureau of Mines did considerable work at pressures below 2,000 psig and at 250°C. However, the products obtained at these mild conditions were pitches instead of oils. The lowest temperature at which a suitable oil could be produced was 300°C, at which temperature the combined water vapor and carbon monoxide pressure exceeded 2,000 psig.

The Bureau of Mines conducted some interesting experiments using formic acid or sodium formate in place of carbon monoxide. This lowered the operating pressure at 250°C to the range of 1,000 - 1,100 psig, and still gave good oil yields, as shown in Table 2 below. This technique would be less successful above 250°C because the formates decompose too rapidly.

Table 2. - Liquefaction of Wood in Absence of Carbon Monoxide

(50 g softwood sawdust 50 g Cresol solvent, 1 hr at 250°C)

| Water, ml | Catalyst, g | | Pressure, psig | Oil yield pct | Conversion pct |
|-----------|--------------------------|---------------------------|----------------|---------------|----------------|
| | Type HCO ₂ Na | Amount HCO ₂ H | | | |
| 100 | 1 | 5 | 1,070 | 60 | 99.6 |
| 100 | 5 | 1 | 1,040 | 55 | 99.0 |
| 100 | 2.5 | 2.5 | 1,050 | 55 | 99.8 |
| 50 | 2.5 | 2.5 | 1,040 | 41 | 90 |

The unstabilized crude wood oil is very reactive to continued exposure to temperature. The Bureau of Mines studied the effect of recycling wood-derived oil. When using an initial carrier oil, such as mixed cresols, it was calculated that after 6 runs, using the product as recycle oil carrier, the original carrier oil would be reduced to about 9 percent. A series of runs at 250°C to 275°C showed that the product became too thick to use after only four cycles. A temperature of at least 300°C and pressures of 2,7000-3,000 psig were needed to obtain a product with acceptable softening point.

OTHER RESEARCH ON BIOMASS LIQUEFACTION

There has been other research on biomass liquefaction by high-pressure, liquid-phase systems, but it appears to be fragmented and scattered. Remarkably, many of the concepts presented by the Bureau of Mines in the early 1970's appear to remain to some extent the "state-of-the-art" in biomass liquefaction, compared for example, with the extensive technology developed for coal liquefaction by Mobil, Exxon, Gulf and others, largely supported by the DOE and some by EPRI.

Battelle Pacific Northwest Laboratories

A fundamental study using pure cellulose (Solka-floc) was performed at Battelle, sponsored by the Division of Chemical Sciences, Processes and Techniques Branch, DOE (3). A series of 129 autoclave experiments analyzed by statistical methods indicated that carbon monoxide, while it promotes the attainment of high yields as claimed by the Bureau of Mines, is not necessary for the reaction to proceed. Analysis of the products by ^{13}C -NMR, GC/MS, and gel permeation chromatography indicated that the non-volatile fraction of the oil consists of 44% aromatic carbon and 7% aromatic hydrogen, corresponding to a benzenoid polyaromatic with a substitution ratio of 5:1. However, the oxygen content of the non-volatile fraction and distillable oil is approximately the same. Since the oil contains a series of polyalkylated furans, this suggests that the char is a poly-furan rather than a conventional asphaltene derivative. Volatile products from the oil fraction consists of furans, cyclic ketones, linear and branched alkenes, and phenolics. The high proportion of phenolics relative to normal crude oil could explain the observed highly corrosive nature of the biomass-derived oils.

Albany Biomass Liquefaction Facility

The Albany facility operated on the basic PERC process, so designated because the original work was conducted at the Pittsburgh Energy Research Center. It was operated initially by the Bechtel Corporation, followed by the Rust Engineering Company (the latter for prime contractor, Wheelabrator Cleanfuel Corporation). The process involved reacting biomass in an oil slurry with carbon monoxide and hydrogen at temperatures up to about 380°C and pressures up to 4,000 psig.

The final Albany test run, Test Run No. 12, prior to shutdown and phaseout on June 30, 1981, produced over 11,000 pounds of wood oil is a sustained and controlled run. The oil had characteristics closely approximating the original design basis as shown below in Table 3.

Table 3 -- Summary of Properties of Albany Crude Wood Oil

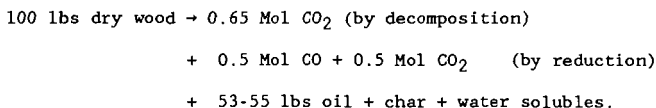
| | <u>Design Basis</u> | <u>Run 12 Product</u> |
|------------------|-------------------------------|-----------------------------|
| Specific gravity | 1.1 | 1.11 |
| Viscosity | 515 cp at 140°F | 135 cp at 210°F |
| Heating value | 13,390 Btu/lb (Calculated) | 14,840 Btu/lb (measured) |

Crude Wood Oil Analysis:

| | | |
|----------|-------|------|
| Carbon | 72.62 | 78.9 |
| Hydrogen | 7.05 | 8.51 |
| Nitrogen | 0.13 | 0.5 |
| Sulfur | 0.14 | 0.08 |
| Oxygen | 20.05 | 12.3 |

Lawrence Berkeley Laboratory (LBL)

This laboratory provided technical assistance to the Biomass Facility at Albany, Oregon. For example, during the earlier period of Albany operations, it provided useful guidance from material balances on what chemical reactions might be occurring (5). It deduced that Douglas Fir wood converted to oil plus small amounts of water-soluble products and char at about 52-55 wt % efficiency. Based on an approximate stoichiometric analysis, the following changes occur.



Carbon monoxide used is about 200 SCF/100 lbs wood or 370 SCF 100 lbs product or 1300 SCF/bbl product. The yield of non-gaseous product can be less than 51% only if carbon monoxide is generated by decomposition of wood or by reaction of wood or its products with water. This appeared to be contrary to observations.

LBL researchers focused their attention on the prehydrolysis of wood to cut down swelling so that wood/water slurries containing up to 25 wt % wood could be pumped (6). This was done at 180°C, 45 min, with 500 ppm sulfuric acid. They used moist chips, water content of 75 wt.% and operated at about pH of 2 in a stirred autoclave. The wood chips disintegrated into fine particles and some courser but friable particles. When the resultant sludge passed through a disc refiner, a pumpable slurry was obtained.

LBL constructed a bench-scale liquefaction unit based upon the above water/oil/wood slurry concept. It was operated with limited success, but ran into plugging problems, possibly due to the small diameter of process tubing. Also, considerable wood oil product dissolved in the large water phase, and the economics of recycling this large water phase or treating it for disposal did not look attractive from the limited experimental data.

Crude Wood Oil Fuel-Burning Tests

Test runs were also made in the Albany facility to simulate the conditions proposed by LBL for its water/oil/wood slurry system, and in fact was the technique that produced the first significant quantities of wood oil. Combustion tests were conducted in a commercial boiler on oils produced by both LBL and PERC process modes at the Pittsburgh Energy Technology Center (PETC). Two barrels, approximately 100 gallons of wood oil from each process, were burned in a 20 Hp Johnson three-pass fire tube boiler designed to transfer 670,000 Btu per hour, with results as follows:

Table 4. Comparison of Heavy Liquid Fuels

| | Test Run No. 8 PERC Distillate Oil | Test Run No. 7 LBL Crude Oil | Fuel Oil No. 2 | Fuel Oil No. 6 |
|-------------------------|---------------------------------------|---------------------------------|-------------------|-------------------|
| Carbon % | 84.5 | 78.1 | 87.3 | 87.0 |
| Hydrogen % | 9.5 | 7.7 | 12.5 | 11.0 |
| Nitrogen % | 0.2 | 0.1 | -- | 0.3 |
| Sulfur % | 0.2 | 0.1 | 0.21 | 0.70 |
| Ash % | 0.2 | 0.2 | -- | 0.10 |
| Oxygen % | 8.4 | 13.8 | -- | 1.0 |
| Heating value Btu/lb | 19,840 | 17,360 | 18,610 | 14,940 |

Upgrading Crude Wood Oil by Hydrotreating

Currently, Battelle Pacific Northwest Laboratory has a major effort on the development of a hydrotreating process for wood oil product upgrading (7,8). Individual components from the product of direct liquefaction of biomass have been subjected to hydrogenation with a number of transition metal oxide catalysts. Sulfided cobalt-molybdenum has been found to be effective for the hydrodeoxygenation of phenolics. The product of choice from hydro-treating would be the aromatic product which maximizes oxygen removal and minimizes hydrogen consumption.

Other Interest in Biomass Liquefaction

This paper emphasized direct biomass liquefaction in the United States, but would be remiss if it did not point out the high interest in biomass liquefaction in other parts of the world, especially Canada and Europe. Low pressure pyrolysis is being investigated at the University of Sherbrooke, Canada (9). At the Royal Institute of Technology, Sweden, a research project in progress compares the dissolution of coal, peat and biomass in hydrogen donor solvent - tetralin at 350°C to 400°C, cold pressure of nitrogen 5.0 MPa and reaction time 15 to 120 minutes (10). At the University of Saskatchewan, Canada, the liquefaction of aspen poplar wood to produce a proto-oil was investigated (11). In the batch reactor studies, the water to wood ratio emerged as the most important parameter affecting yield and quality of oil. The Department of Scientific and Industrial Research, New Zealand, believes that biomass liquefaction has several inherent advantages over other processes for obtaining liquid fuels (12). The process is rapid and it does not require the production of reducing gases. This should allow smaller scale processing than other processes. Biomass is much less abrasive, and it is softer than coal.

CURRENT BIOMASS LIQUEFACTION RESEARCH AT ARIZONA

The advanced extruder-feeder biomass liquefaction reactor system was designed to experimentally convert wood flour to liquid wood oil fuels by direct liquefaction. The extruder-feeder system developed at the University of Arizona is incorporated into the system to develop 3,000 psig pressure at its discharge and preheat the slurry prior to entering the vertical reactor. As the wood flour slurry enters the reactor it is mixed with superheated steam and carbon monoxide. Gas dispersion as well as heat and mass transfer will be attempted by the use of static mixer elements inside the tubular reactor. The superheated steam is used to heat the wood flour slurry up to the reaction temperature of 350°C almost instantaneously, which is then maintained by the use of electrical band heaters surrounding the reactor. Steam and carbon monoxide also react via the water-gas shift reaction to provide hydrogen for the liquefaction. The liquefaction products are split into the vapor and liquid

fractions, condensed, cooled down and brought to atmospheric pressure by means of the let-down system. Computer control and real-time data acquisition have been implemented for the unit.

The University of Arizona in its limited experimental runs over the past year has consistently produced a low-oxygen crude wood oil, namely, in the 6-8 wt % oxygen range. A few samples of this oil are currently being evaluated for upgrading by hydrotreating by Battelle Pacific Northwest Laboratory (13). This may prove to be a good candidate of wood oil for upgrading to a petroleum-like transportation fuel.

Experimental data for some of the initial runs made at the University of Arizona over the period of August 29, 1985 through July 2, 1986 are shown in Tables 5, 6 and 7. These experimental runs were purposely planned to cover several extremes of operating conditions, namely, pressure, with and without reactant carbon monoxide, and with and without sodium carbonate catalyst. Experimental runs showing effects of residence time, temperature and various feedstock treatments have not yet been performed.

Table 5 -- Continuous Biomass Liquefaction Experimental Conditions

| Run No. | Wood Four | Wood Oil Vacuum Bottoms | Feedstock H ₂ O, wt. % | Na ₂ CO ₃ Catalyst, pp hr. | Temp. °C | Press. psi | Feed Rate lb/hr | Residence Time Minutes |
|---------|-----------|-------------------------|-----------------------------------|--|----------|------------|-----------------|------------------------|
| 1 | 40 | 60 | 8 | 10 | 375 | 3,000 | 10 | 72 |
| 2 | 38 | 62 | 12.2 | 2 | 400 | 800 | 6 | 120 |
| 3 | 38 | 62 | 8.8 | 0 | 400 | 1,000 | 8 | 90 |
| 4 | 38 | 62 | 15 | 0 | 400 | 1,200 | 7 | 103 |
| 5 | 40 | 60 | 19.7 | 0 | 400 | 2,300 | 10 | 72 |
| 6 | 38 | 62 | 15 | 2 | 400 | 3,000 | 3 | 240 |
| 7 | 40 | 60 | 15 | 0 | 400 | 3,000 | 8 | 90 |

Table 6 -- Elemental Analysis of Crude Wood Oil Obtained by Liquefaction

| Run No. | Crude Distillate, wt. % | Crude Distillate Analysis, wt. % | | | |
|---------|-------------------------|----------------------------------|------|-------|------|
| | | C | H | O | N |
| 1 | 24.8 | 82.71 | 9.07 | 6.52 | 0.13 |
| 2 | 24.7 | 84.72 | 9.03 | 9.03 | 0.22 |
| 3 | 39.0 | 84.51 | 8.66 | 8.66 | 0.22 |
| 4 | 27.0 | 84.12 | 8.67 | 8.67 | 0.34 |
| 5 | 23.4 | 82.00 | 8.81 | 8.81 | 0.21 |
| 6 | 30.0 | 81.64 | 8.46 | 8.90 | 0.10 |
| 7 | 27.0 | 80.00 | 8.40 | 10.02 | 0.00 |

Table 7 -- Properties of Crude Wood Oil Obtained by Liquefaction

| Run No. | Viscosity, C.S., 30°C | Heat of Combustion Btu/lb. | Water Content mg./mol | Aromacity (NMR) | |
|---------|-----------------------|----------------------------|-----------------------|-----------------------|------|
| | | | | Aromatic/Aliphatic, C | H |
| 1 | 86 | 16,300 | 3.08 | 0.60 | 0.22 |
| 2 | 135 | 16,960 | 3.19 | 0.68 | 0.32 |
| 3 | 164 | 16,510 | 5.51 | 0.68 | 0.30 |
| 4 | 155 | 16,450 | 7.71 | 0.66 | 0.27 |
| 5 | 100 | 16,200 | 5.43 | 0.69 | 0.37 |
| 6 | 120 | 16,020 | 5.48 | 0.88 | 0.31 |
| 7 | 103 | 15,000 | 8.69 | 0.99 | 0.36 |

The crude distillate was obtained by vacuum distillation of the reactor effluent at 2-3 mm/Hg absolute pressure and temperatures starting at about 300°F and going up to 550°F. As can be seen it has a reasonably low viscosity at 30°C and a heat of combustion of about 16,000 BTU/lb. The aromatic content as determined by nuclear magnetic resonance is about 40 percent. Most important, the oxygen content has been reduced during liquefaction from about 42 wt.% in the white birch feedstock to about 6-7 wt.%, such that hydrotreating to a transportation fuel should be facilitated.

Even though the extruder-feeder has demonstrated the ability to feed 60 wt.% wood flour/sawdust feedstocks, these initial experimental runs were made with feedstocks ranging from 35 to 42 wt.% white birch wood flour. Thus, if one assumes the heavy vacuum bottoms are essentially inert as a carrier of the feedstock, then one would expect to generate 35 to 40 wt.% (less losses due to oxygen reduction) of crude wood oils in the once-through liquefaction system. Some results to date on the vacuum distillation of the reactor effluent, which contains the Albany vacuum bottoms carrier are as follows:

Table 8 -- Vacuum Distillation of Liquefaction Reactor Crude Product

| Run No. | Run Date | Feedstock W.F., wt. % | Reactor Pressure psi | Percentage of Reactor Product Distilled, wt. % | Percentage of Reactor Product Condensed, wt. % |
|---------|----------|-----------------------|----------------------|--|--|
| 2 | 2/19/86 | 36 | 800 | 24.7 | 17.5 |
| 3 | 3/19/86 | 38 | 1,000 | 39.0 | 25.5 |
| 4 | 4/19/86 | 38 | 1,200 | 27.0 | 19.0 |
| 5 | 5/29/86 | 40 | 2,300 | 23.4 | 16.0 |
| 6 | 6/30/86 | 36 | 3,000 | 30.0 | 20.0 |
| 7 | 7/02/86 | 40 | 3,000 | 27.0 | 23.9 |
| 8 | 7/30/86 | 33 | 600 | 19.0 | 9.0 |
| 9 | 7/31/86 | 33 | 600 | 20.0 | 11.0 |

The liquefaction of wood to a crude wood oil having a much lower oxygen content and essentially little change in the hydrogen content means that for even a 100% of theoretical conversion to wood oil, there is a large loss of weight of product compared with the feedstock weight. Under certain liquefaction conditions, the elimination of oxygen from wood can occur by about 60 percent as water and 40 percent as carbon dioxide (14). Under other liquefaction conditions, the elimination of oxygen from wood is claimed to occur by about five percent water and 95 percent carbon dioxide (15). The off-gas of the above experimental runs were analyzed, but due to the water present from the steam injection, the ratio of water/carbon dioxide evolved from white birch wood has not yet been determined. Assuming a 50/50 ratio of

water/carbon dioxide evolving in these data, the theoretical loss of weight of wood going from 41.26 wt.% oxygen to 7.0 wt.% oxygen is 48 percent. Thus, 100 pounds of dry white birch biomass can theoretically produce about 52 pounds of crude wood oil, under the above assumption of liquefaction conditions. If one were to apply this theoretical yield to the amount of condensed distillate obtained as listed in Table 8, then yields greater than 100 percent theoretical are obtained. Even changing the assumption on the ratio of water/carbon dioxide rejection from the biomass over a range consistent with known H/C ratios of crude wood oils can only partially account for the high quantities of crude oil distillates obtained. One other conclusion that could be drawn (assuming the experimental data is reasonably correct) was that the Albany black vacuum bottoms are not inert at the liquefaction temperature of 375-400°C. Consequently, the thermal stability and possibility of obtaining distillable products from the Albany black vacuum bottoms were investigated.

The Albany black vacuum bottoms used at the University of Arizona came in drum lots from Albany, Oregon, where it was obtained by fractionating Douglas Fir wood oil in a fairly large vacuum fractionator. This material was used during the period August 29, 1986 through July 2, 1986 until essentially exhausted. A second lot of Albany vacuum bottoms, a brownish-black in color, was used in a "long run" of 52 hours duration conducted July 29-31, 1986. The elemental analysis of these two Albany vacuum bottoms and some related data are as follows:

Table 9 -- Elemental Analyses Related to Feedstocks and Carrier Oils

| | Wt. % C | Wt. % H | Wt. % O | Wt. % N | Total CHON |
|-----------------------|---------|---------|---------|---------|------------|
| Black Vacuum Bottoms | 78.96 | 6.71 | 12.05 | 0.26 | 97.98 |
| Brown Vacuum Bottoms | 81.58 | 6.25 | 9.22 | 0.37 | 97.42 |
| Distillate Black V.B. | 85.21 | 7.60 | 5.32 | 0.23 | 98.36 |
| White Birch Wood | 46.98 | 5.61 | 41.26 | 0.04 | 93.89 |

First, to test the thermal stability of black vacuum bottoms, a series of three samples were heated in the absence of other reactants to 400°C for 2, 3 and 4 hours, respectively, in a pressure autoclave. The autoclave was cooled, all products except gases collected, and analyzed. Whereas the fresh Albany black vacuum bottoms were 99-100% soluble in THF, all three of the samples heated to 400°C for 2 to 4 hours showed that in all three cases 50 percent of the original samples were insoluble in THF, indicating a further cross-linking, polymerization, oxidation or carbonization of some type. Equally important, the other 50 wt.% of the original sample appeared to represent about 7 wt.% off-gas at 400°C and about 43 wt.% remaining as a "vacuum bottoms" containing some crude wood oil.

Secondly, when the fresh Albany black vacuum bottoms are further distilled at 2-3 mm/Hg absolute pressure, a total of 22.5 wt.% distilled as the temperature gradually was raised to 550°F, at which point no additional distillate was observable. A total of 16.3 wt.% of the original feed was condensed with 70°F cooling water with the balance being non-condensables at 70°F.

Yields of crude wood oil appear to be from 80 to 100 percent of the theoretical when all of the above data are used in the calculations. The weakest assumptions involve how much additional crude wood oil is derived from the Albany black vacuum bottoms carrier fluid. Another indication of the near-theoretical yield of crude wood oil is the low methane, ethane and hydrogen content of the off-gas, despite the liquefaction temperature being on the high side at 375-400°C.

CONCLUSIONS

A reasonably low-viscosity, low-oxygen crude wood oil can be obtained in the once-through, near-plug flow high-concentration solids vertical reactor system. Experimental conditions to date are on the high side of temperature and residence time, and on the low side with respect to pressure, quantity of steam, quantity of sodium carbonate catalyst, quantity of carbon monoxide reactant and quantity of superheated steam. The experimental unit exhibits good operability and has begun to provide good material balances, such that it appears that future runs can evaluate the many parameters affecting conversion, yield and quality of the crude wood oil.

REFERENCES

1. Appell, H.R. et al., "Converting Organic Wastes to Oil", BuMines RI 7560 (1971).
2. Appell, H.R. et al., "Conversion of Cellulosic Wastes to Oil", BuMines RI 8013 (1975).
3. Molton, P.M. et al., "Mechanism of Conversion of Cellulosic Wastes to Liquid Fuels in Alkaline Solution", Presented at Third Energy from Biomass and waste Symposium, Sponsored by IGI, Held at Alexandria, Virginia (August 1978).
4. Berry, W.L. and P.L. Thigpen, "Operation of the Biomass Liquefaction Facility, Albany, Oregon", Presented at 13th Biomass Thermochemical Conversion Contractor's Meeting, Arlington, Virginia (October 1981).
5. Davis, H. et al., "Catalytic Biomass Liquefaction Quarterly Report" LBID-272, Lawrence Berkeley, Berkeley, California (April-June, 1980).
6. Ergun, S. et al., "Catalytic Biomass Liquefaction Quarterly Report", LBL-11019, Lawrence Berkeley Laboratory, Berkeley, California (February 19, 1980).
7. Elliott, D.C., "Bench Scale Research in Biomass Direct Liquefaction", Presented at the 14th Biomass Thermochemical Conversion Contractor's Meeting, Arlington, Virginia (June 1982).
8. Elliott, D.C., "Hydrotreating Biomass Crude Oils", Proceedings Annual Biomass Thermochemical Conversion Contractors Meeting, Minneapolis (October 1985).
9. Roy, C. C. et al., "The Pyrolysis under Vacuum of Populus Tremuloides and its Constituents", Presented at Fundamentals of Thermochemical Biomass Conversion: An International Conference, Estes Park, Colorado (October 1982).
10. Hornell, C. et al., "Dissolution of Peat and Wood in Tetralin compared with Coal", Presented at Fundamentals of Thermochemical Biomass Conversion: An International Conference, Estes Park, Colorado (October 1982).
11. Eager, R.G., et al., "Liquefaction of Aspen Poplar to Produce an Oil and Chemicals", Presented at Fundamentals of Thermochemical Biomass Conversion: An international Conference, Estes park, Colorado (October 1982).
12. Miller, I.J., "Biomass Liquefaction as a Potential Process", Presented at Fundamentals of Thermochemical Biomass Conversion: An International conference, Estes Park, Colorado (October 1982).
13. White, D.H., Personal Communication with D.C. Elliott (August 1, 1986).
14. Espenscheid, W.F., "Liquefaction of Solid Carbonaceous Materials", U.S. Patent 4,052,292 (October 4, 1977).

15. Chen, N.Y. et al., "Liquefaction of Solid Carbonaceous Materials", U.S. Patent 4,247,384 (Issued January 27, 1981).

ACKNOWLEDGEMENT

This research was supported by Department of Energy Contracts DE-AC06-76RLO-1830 (Subcontract B-96249-A-Q from Battelle Pacific Northwest Laboratories) and DOE Contract EW-78-S-05-5679. Special thanks are given to M. Chehab, A. Homaïdon, A. Lezzar, D. Joshi and B. Reyes, who performed much of the experimental work. We also appreciated the assistance of Professor N.R. Schott, while on Sabbatical at the University of Arizona. Many undergraduate students too numerous to list have also contributed to this research project and their help is greatly appreciated.